



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :  <b>C04B 12/00</b>		A1	(11) International Publication Number: <b>WO 93/16965</b>  (43) International Publication Date: 2 September 1993 (02.09.93)
(21) International Application Number: PCT/GB93/00373  (22) International Filing Date: 23 February 1993 (23.02.93)		(74) Agents: FUNGE, Harry et al.; M'Caw & Co., 41-51 Royal Exchange, Cross Street, Manchester M2 7BD (GB).	
(30) Priority data: 92/1457 27 February 1992 (27.02.92) ZA		(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).	
(71) Applicants: PRETORIA PORTLAND CEMENT COMPANY LIMITED [ZA/ZA]; 11 Sherborne Road, Parktown, 2193 Johannesburg (ZA). GOMERSALL, John, Edward [GB/ZA]; 63, Mount Street, Bryanston, 2021 Sandton (ZA).		Published <i>With international search report.</i>	
(72) Inventor: FOUCHÉ, Pierre, Marc ; 63, Kammanassie Street, Brackendowns, 1450 Alberton (ZA).			

## (54) Title: GEOPOLYMERIC BINDER MATERIAL

## (57) Abstract

A dry composition suitable for use as a binder upon being mixed with water, the composition comprising a mixture of an alkaline earth metal compound selected from the group consisting of the oxides and hydroxides of calcium and magnesium, a salt of a cation selected from the group consisting of ammonium, potassium and sodium which is capable of reacting with the alkaline earth metal compound to produce the hydroxide of the cation, a source of silica and a source of an alumina silicate.

***FOR THE PURPOSES OF INFORMATION ONLY***

**Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.**

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	IU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam

-1-

## GEOPOLYMERIC BINDER MATERIAL

THIS invention relates to compositions of matter of the type known in the trade as binder and more particularly geopolymeric binders. The term "geopolymeric" is understood in the trade as referring to a material which is composed of or which includes a binder component which has the general chemical formula  $(\text{Si-O-Al-O-})_n$ , [also known as polysialates], and  $(\text{Si-O-Al-O-Si-O-})_n$ , [also known as polysialatesilioxos].

It is known to produce geopolymers of the type in question by reacting a sodium or potassium silicate solution with an aluminium bearing source material, such as an alumina rich clay, and incorporating a filler material, such as sand and/or stone aggregate into the mixture to produce a castable or mouldable material which may be used in the same manner as cement or concrete. Since the alkali metal silicate contains a large percentage water it is in these applications normally preferred to form the silicate on site by reacting sodium or potassium hydroxide with silica gel  $[\text{SiO}_2]$ . The product of choice in this regard is sodium hydroxide which is not only very corrosive, but also hygroscopic and expensive. These considerations are at least in part responsible for the low penetration of geopolymers into the conventional porcelanic cement market which cement is based on hydrated calcium silicates.

-2-

It is an object of the present invention to provide a dry composition of matter in a form ready to mix with water and filler material and suitable for use as a binder material, e.g. as a conventional cement 5 substitute. It will however be appreciated that the composition may also find various other applications.

According to the present invention there is provided a dry composition suitable for use as a binder upon being mixed with water, the composition comprising a mixture 10 of an alkaline earth metal compound selected from the group consisting of the oxides and hydroxides of calcium and magnesium, a salt of a cation selected from the group consisting of ammonium, potassium and sodium which is capable of reacting with the alkaline earth 15 metal compound to produce the hydroxide of the cation, a source of silica and a source of an alumina silicate.

In one form of the invention the cation salt is selected from the group consisting of the carbonates and hydrocarbonates of ammonium, potassium and sodium, 20 ammonium chloride and ammonium nitrate. In the preferred form of the invention the salt is sodium carbonate. Also in the preferred form of the invention the alkaline earth metal compound is calcium hydroxide.

25 The source material of silica and the alumina silicate may be a single composite material. Thus, that source

-3-

material may be in the form of an alumino-silicaceous clay. Alternatively, the source may comprise powdered blast furnace slag.

In the preferred form of the invention the source 5 material may at least in part be constituted by fly-ash. The composition may in addition also include other sources of silica such as, for example, fumed silica condensate.

In the mixture of the composition according to the 10 invention the ingredients may be present in the following stoichiometric equivalent mole ratio:

Alkaline earth metal oxide/hydroxide	1 - 1,2
Cation salt	1
Fly-ash	1
15 SiO <sub>2</sub> [fumed silica condensate]	1 - 3

Thus, in one specific formulation according to the invention the ingredients may be present in the following mass ratio:

Sodium carbonate	10 - 35 parts
20 Calcium hydroxide	10 - 50 parts
SiO <sub>2</sub>	20 - 80 parts
Fly-ash	50 - 120 parts [depending on the amount of reactive alumina

-4-

silicate present therein]

A preferred composition of this formulation according to the invention comprises the following ingredients in the mass ratio as indicated:

5	Sodium carbonate	24 parts
	Calcium hydroxide	38 parts
	Fumed silica condensate	60 parts
	Fly-ash	100 parts

10 The dry composition of the invention may be made into a binder material by mixing it with between 20 and 50 parts of water.

15 Thus, in the preferred composition comprising 24 parts of sodium carbonate as described above, the dry mix is preferably made up into a wet mix by the addition of 40 parts of water. Sand may be worked into the mix either before or after the addition of water. In accordance with a specific aspect of the invention, however, it is preferred to make up the dry mix with water and thereafter to work the wet mix into up to 300 parts of sand.

20 According to a second aspect of the invention there is provided a two pack binder mixture comprising a first pack made up of the alkaline earth metal compound, the

-5-

cation salt as defined above and the silica, and a second pack containing the source of alumina silicates.

An example of the invention will now be described without thereby limiting the scope of the invention.

5

E X A M P L E 1

A dry mix of powdered ingredients was made up as follows:

		<u>Parts by mass</u>
	Sodium carbonate [NaCO <sub>3</sub> ]	- 24
10	Calcium hydroxide [Ca(OH) <sub>2</sub> ]	- 30
	Silica [Fumed silica condensate] SiO <sub>2</sub>	- 60
	Fly-ash	- 100

The fly-ash used in the mixture was Class F fly-ash obtained from Matla power station in the Eastern Transvaal, South Africa and would accordingly have had the following typical composition and ignition properties.

	<u>Constituent</u>	<u>% by Mass</u>
	SiO <sub>2</sub>	40,04 - 50,6
20	Al <sub>2</sub> O <sub>3</sub>	26,30 - 38,93

-6-

	Fe <sub>2</sub> O <sub>3</sub>	2,63 - 5,55
	CaO	4,42 - 12,80
	MgO	1,15 - 3,10
	SO <sub>3</sub>	0,16 - 1,13
5	Na <sub>2</sub> O	0,30 - 1,03
	K <sub>2</sub> O	0,20 - 0,99
	Loss upon Ignition	0,80 - 3,86

Two test cubes were produced from the above mixture.

In the first instance the four components set out above  
10 were thoroughly mixed first on their own and then with  
300 parts of sand. 40 Parts of water were then added  
to the mixture to obtain a wet mix. The wet mix was  
introduced into a vibrating cubic mould and allowed to  
set at room temperature. After curing the moulded cube  
15 at room temperature for 7 days it was found that the  
cube had a compressive strength of more than 15 mPa.

In the second instance the Na<sub>2</sub>CO<sub>3</sub>, Ca(OH)<sub>2</sub> and SiO<sub>2</sub> was  
first mixed with 40 parts of water whereafter the  
fly-ash was added and thoroughly mixed. The resulting  
20 slurry was then added to the sand [300 parts] and again  
thoroughly mixed. A cube was produced as described  
above and was found after 7 days of curing to have a  
compressive strength of between 18 and 30 mPa.

Countless variations of the invention may be devised

- 7 -

without departing from the spirit of the invention.

-8-

## Claims

1. A dry composition suitable for use as a binder upon being mixed with water, the composition comprising a mixture of an alkaline earth metal compound selected from the group consisting of the oxides and hydroxides of calcium and magnesium, a salt of a cation selected from the group consisting of ammonium, potassium and sodium which is capable of reacting with the alkaline earth metal compound to produce the hydroxide of the cation, a source of silica and a source of an alumina silicate.
2. The composition of claim 1 wherein the cation salt is selected from the group consisting of the carbonates and hydrocarbonates of ammonium, potassium and sodium, ammonium chloride and ammonium nitrate.
3. The composition of claim 1 wherein the cation salt is sodium carbonate.
4. The composition of claim 1 wherein the alkaline earth metal compound is calcium hydroxide.
5. The composition of claim 1 wherein the source material of silica and the alumina silicate is a single composite material material in the form of an alumino-silicaceous clay or a powdered blast

-9-

furnace slag.

6. The composition of claim 1 wherein the silica and alumina silicate source material is at least in part constituted by fly-ash.

5 7. The composition of claim 6 which in addition also includes fumed silica condensate.

8. The composition of claim 1 wherein the ingredients are present in the following stoichiometric equivalent mole ratio:

10 Alkaline earth metal oxide/hydroxide 1 - 1,2  
Cation salt 1  
Fly-ash 1  
SiO<sub>2</sub> [fumed silica condensate] 1 - 3

9. The composition of claim 8 wherein the ingredients are present in the following mass ratio:

Sodium carbonate 10 - 35 parts  
Calcium hydroxide 10 - 50 parts  
SiO<sub>2</sub> 20 - 80 parts  
Fly-ash 50 - 120 parts

25 10. The composition of claim 1 in the form of a two pack binder mixture comprising a first pack

-10-

containing of the alkaline earth metal compound, the cation salt as defined above and the silica, and a second pack containing the source of alumina silicates.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00373

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C04B12/00

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.C1. 5	C04B

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,2 490 626 (J. DAVIDOVITS ET AL) 26 March 1982 see page 2, line 41 - page 3, line 47 see page 5, line 16 - line 42; claims 1,4,6	1-5
Y	---	6-7
Y	EP,A,0 455 582 (HILTI AG) 6 November 1991 see page 1, line 16 - page 2, line 20 see page 3, line 49 - page 4, line 16 see claims 1-6; examples 1,7; table 2 ---	6-7
X	EP,A,0 262 302 (ANNELIESE ZEMENTWERKE AG) 6 April 1988 see abstract; claims 1-2 see column 3, line 11 - column 4, line 7 ---	1-5
		-/-

<sup>10</sup> Special categories of cited documents :

- <sup>A</sup> document defining the general state of the art which is not considered to be of particular relevance
- <sup>E</sup> earlier document but published on or after the international filing date
- <sup>L</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- <sup>O</sup> document referring to an oral disclosure, use, exhibition or other means
- <sup>P</sup> document published prior to the international filing date but later than the priority date claimed

<sup>T</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>X</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>Y</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>&</sup> document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

28 MAY 1993

Date of Mailing of this International Search Report

14.06.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

OLSSON S.A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	GEOPOLYMER '88 vol. 1, pages 93 - 105 J. DAVIDOVITS 'Geopolymeric reactions in archaeological cements and in modern blended cements' & CONCRETE INTERNATIONAL vol. 9, December 1987, USA pages 23 - 29 see page 98, line 16 - page 99, line 23 see page 101, line 4 - page 102, line 14 ---	1-5
X		1-5
A	US,A,4 642 137 (R. F. HEITZMANN ET AL) 10 February 1987 see abstract; claims 1,6,11-12 see column 1, line 41 - column 2, line 18 see column 3, line 57 - column 4, line 24; example 1 -----	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

GB 9300373  
SA 70978

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28/05/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2490626	26-03-82	None		
EP-A-0455582	06-11-91	DE-A- 4009998 JP-A- 4228463		02-10-91 18-08-92
EP-A-0262302	06-04-88	DE-A- 3633736		14-04-88
US-A-4642137	10-02-87	AU-B- 587638 AU-A- 6355886 JP-B- 4043863 JP-A- 63112444		24-08-89 14-04-88 17-07-92 17-05-88